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THERMAL AND FT-IR ANALYSIS OF THE POLYURETHANE FOAMING REACTION

THE EFFECT OF THE ISOCYANATE INDEX

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INTRODUCTION

The polyurethane-forming reaction was initially patented about fifty years ago. From this idea evolved a technology for making a wide variety of products of which flexible and rigid foams are the most notable. They result from the combination of multifunctional isocyanates and polyols, silicone surfactants and catalysts. These complex systems still offer a challenge to the understanding of those working in the field as witnessed by numerous recent publications and monographs (1-8).

Recently we reported on the fate of residual isocyanate in foams obtained with a wide range of indices (6). Here, we study the effect of isocyanate index upon the exotherm curve as well as on the foam composition as determined by FT-IR spectroscopy immediately after the reaction.

EXPERIMENTAL

Materials and Foaming Procedure

The materials and foaming procedure are similar to those reported previously (6). Briefly, NIAX Polyol 16-46 (500 g, Union Carbide Canada Ltd.), water (20 g), NIAX Catalyst A-1 (0.5 g, Union Carbide Corp.), Union Carbide Silicone Surfactant L-6202 (5.0 g) are mixed for 60 s. The mixing is stopped while the stannous octoate (1.25 g, Air Products and Chemicals, Inc.) is added. The mixing is resumed for a final 15 s. The 80/20 TDI (varying amounts, BASF) is added 6 s before the end of mixing. Five minutes after the end of mixing the foam buns are cured for 10 min in an oven at 70°C. The foam buns are left to cool at 50% relative humidity and 22°C before FT-IR analysis.

Exotherm Measurements and Parameters

Computer data acquisition of exotherms has been described (8). Here, temperature measurements were performed with a very fine (0.010") Chromel-Constantan thermocouple fed via an analog/digital converter to an IBM PC-XT computer. "Asystant" software (Asyst Software Technologies, Inc.) allowed the generation of curves showing the variation with time of both the temperature and its derivative with respect to time (Fig. 1). A number of relevant parameters can be extracted (9) from these curves, for instance:

dT/dt_1 = maximum rate of temperature rise for the first ("blowing") reaction

dT/dt_2 = maximum rate of temperature rise for the second ("gelling") reaction

dT/dt_3 = maximum rate of temperature rise for the third reaction

t_1, t_2, t_3 = times to reach these maxima

$T_{max\ A}$: maximum temperature attained for the first plateau (after dT/dt_1 and dT/dt_2)

$T_{max\ B}$: maximum temperature attained for the second plateau (after dT/dt_3)

Infrared Spectroscopy

FT-IR spectra of foams were measured by attenuated total reflection (ATR) on a Nicolet 170SX instrument equipped with a liquid-nitrogen-cooled mercury cadmium telluride detector. The ATR accessory was a Twin Parallel Mirror Attachment from Harrick Scientific Corporation with a 45° KRS-5 single pass parallelogram prism (50 x 10 x 3 mm). Each spectrum was an accumulation of 128 scans, requiring about 80 s. The resolution used was 4 cm^{-1}.

For each foam sample, four pieces about 50 x 10 x 5 mm were cut from the centre of the bun with an electric knife. This allowed measurement of two different spectra for each foam, since each spectrum requires two pieces, one on each side of the prism. After the instrumental "background" was recorded using the prism alone, the first set of foam specimens was installed and the throughput measured and the ratio taken against the background to obtain the ATR spectrum. This was followed by measurement of the second set of specimens. Typical time lapses involved were 90 min between foam formation and first cut, 7 min between first cut and first spectrum, 3 min between first spectrum and second spectrum.

For detailed comparison and quantitative analysis, the spectra obtained were "standardized" by means of the following manipulations: (i) conversion to pseudoabsorbance units ($A = -\log_{10} R$); (ii) where necessary, correction for atmospheric CO_2 and water vapour peaks by subtraction of appropriate reference spectra; (iii) baseline correction using the 4000-3600 cm^{-1} and 1750 cm^{-1} regions as reference points; (iv) multiplication of the corrected spectrum by $1000/\nu$, where ν is the frequency in wavenumbers, to correct for

the variation of penetration depth with wavelength in ATR, and thus give a spectrum similar to the transmission spectrum; (v) normalization to give a spectrum in which the maximum absorbance (corresponding to the polyol C-O stretching peak at 1089 cm^{-1}) is equal to 1. This step takes account of variations in overall intensity resulting from differences in the degree of contact between foam and prism.

In the case of samples other than foams, liquids were measured either in transmission between KBr windows, or by ATR using a Prism Liquid Cell (ZnSe prism) from Harrick Scientific Corporation; powders were mixed with KBr and measured by diffuse reflection using a "praying mantis" Accessory, also from Harrick Scientific.

RESULTS AND DISCUSSION

Exotherm Results

The variations of the exothermic parameters in response to a variation of the isocyanate index are shown in Figures 2-4. It was known that temperature in a foaming mass reaches a plateau at about 140-150°C for the formulation tested. Careful observation shows the emergence of a second plateau at an index of 105 (Fig. 2). As the index increases, the second plateau becomes more prominent. Whereas the time of occurrence of the first plateau remains fairly constant at roughly 160 seconds for the whole index range, the occurrence of the second plateau is progressively later at the higher indices.

In Figure 3, the values of the maximum rates of temperature rise (dT/dt_n) for the three distinct peaks in the derivative curve are plotted as a function of the isocyanate index. The rate of the blowing reaction (peak 1, dT/dt_1) increases slowly as the index increases. The rate of the gelling reaction (peak 2, dT/dt_2) on the other hand increases dramatically as the index increases. At index 105 and higher, a third surge in the rate of temperature rise (dT/dt_3) becomes apparent. The rate of temperature rise for this third surge remains nearly constant over the index range where it was observed (I: 105 to 135). This third peak is sharp and well defined in the range 110 to 120. At higher indices the peak progressively broadens (Fig. 4).

The times (t_n) to reach the maxima (dT/dt_n) in the derivative traces are shown in Figure 5 as a function of isocyanate index. The blowing reaction attains a maximum rate (peak 1) sooner for low indices than for high indices. The time of occurrence of the maximum for the rate of the gelling reaction (peak 2) appears unaffected over the index range studied. The third maximum of temperature rise (peak 3) occurs progressively later as the index increases. The pattern formed (Fig. 2-5) by these exotherm parameters is consistent with what urethane producers know very well already: the foaming gets more vigorous as the index increases.

The blowing and gelling reactions in these foams have been associated with the first two maxima in the rates of temperature rise (9). The third maximum in the derivative trace corresponds to the emergence of a second temperature plateau occurring well after the first plateau has been established and long after the foam has stopped rising. It may seem unusual to expect reactions this late in the foaming process, but an increase in temperature has to come from an exothermic chemical reaction.

Such a reaction might be an oxidation reaction but none of the foams produced at the higher indices showed signs of discoloration or scorching. Oxidation products would also be expected to be seen by infrared. We did not observe such products. An alternate explanation was sought in isocyanate-induced cross-linking reactions.

The heats of reaction for the formation of various chemical structures likely involved in water-blown polyurethane foam are shown in Table 1 (2,10). The question is whether it is possible to relate the third exothermic peak to biuret and/or allophanate formation.

TABLE 1.

HEATS OF REACTION

Product	k cal/mole
Urea	45
Urethane	24
Biuret	10
Allophanate	6-7

When the TDI concentration is increased, cross-linking reactions through biuret and allophanate formation can become important. Biuret formation is generally thought to be faster than allophanate formation (5,7,11,12). Furthermore, biuret is expected to be favored compared to allophanate since the concentration of urea N-H groups exceeds by a factor of five that of urethane N-H groups. The spectroscopic evidence presented later also points to the biuret cross-link.

The third peak is only seen beyond a critical TDI excess. Below index 105, a third peak is never seen. While this excess TDI increases the intensity of the first two reactions over the whole range observed, the rate of temperature rise of the third peak remains nearly constant. However the time over which it occurs gradually increases with index as shown by the broadening of the peak (Fig. 4). This, we believe, is because the third reaction occurs in the solid state. While the first two peaks occur during the rise of the foam and its initial gelling, the third comes after the 150°C plateau has occurred. At

this stage the foam has solidified. This renders the already less vigorous exothermic cross-linking reactions more sluggish (Table 1). Two effects are competing. Beyond index 105 sufficient excess isocyanate is present to allow the build-up of cross-links through an exothermic reaction. On the other hand, although cross-links are favored by increasing TDI concentration, they also begin to hinder chain mobility necessary to sustain the reaction. This is consistent with the time dependence of the third derivative peak in Figures 3 and 5 where the maximum is seen to occur at and over progressively longer times as a function of index.

Spectroscopic Results

A) Simple Systems

To aid in interpreting the foam spectra, a number of experiments were done using simpler model systems. The purpose of these was to establish the identity of the main peaks in the foam spectra.

In the first experiment, a mixture of TDI and N.P. 16-46 polyol was prepared with a TDI index of 105, without addition of water, surfactant, or catalysts. Under these conditions, reaction is slow and the mixture remains liquid for some time. IR spectra were measured by ATR immediately after mixing and also one day later. Figure 6 shows the two spectra as well as the curve obtained on subtracting the first from the second. In the mixture spectra, the dominant peaks are the C-H stretching bands at 3000-2800 cm^{-1} (mainly from the polyol), the isocyanate NCO stretching peak at 2257 cm^{-1}, and the polyol C-O stretching band at 1097 cm^{-1}. The difference spectrum shows some quite well-defined peaks which correspond to the changes occurring on reaction. The strong negative peak at 2247 cm^{-1} results from the disappearance of isocyanate groups, whereas the many positive peaks may be assigned to the newly-formed urethane linkages. These peaks occur at 3302 (N-H stretching), 1729 (carbonyl stretching), 1540, 1224, and 1066 cm^{-1}. The last three correspond to mixed modes involving N-H deformation, C-N stretching, and C-O stretching. There is also a peak at 1596 cm^{-1} which is probably a new aromatic ring stretching vibration resulting from the change in symmetry on urethane formation.

In the second experiment, the same polyol was reacted with phenyl isocyanate with stannous octoate as a catalyst. In this case, since the isocyanate is monofunctional, the product remains liquid even when the reaction is carried to completion. Two isocyanate/polyol ratios were used, corresponding to TDI indices of 100 and 125. The spectra are shown in Figure 7. Both show peaks (indicated by arrows) which are not observed in either the polyol or the phenyl isocyanate, and which may be attributed to urethane groups. The most important occur at 3306, 1730, 1543, and 1224 cm^{-1}, in excellent agreement with the previous experiment. In the case of the sample with index 125, some residual isocyanate is present as shown by the peak at 2260 cm^{-1}. The carbonyl peak near 1730 cm^{-1} is particularly interesting since a number of vibrations have been assigned to this region (urethane, allophanate, biuret, etc. (13-20)). Figure 8 shows this peak in greater detail. Although the maximum occurs at 1730 cm^{-1}, there is a shoulder at lower frequency. When

the two spectra are subtracted it is impossible to make this peak disappear completely by adjusting the subtraction factor. Instead, a weak residual peak remains at 1709 cm^{-1}, corresponding to the shoulder just mentioned. This peak could be due either to allophanate groups, formed in greater numbers when the TDI index is higher, or else to hydrogen bonded urethane carbonyl groups (4, 21).

The third experiment was performed in order to produce a sample with only urea groups. TDI and water were reacted in proportions corresponding to an index of 85. The resulting product was a dry, very friable solid, whose spectrum was measured by diffuse reflection (Fig. 9). Based on the findings of Hauptmann (14,15) the carbonyl peak at 1703 cm^{-1} may be assigned to urea groups in a highly disordered environment ("dissolved" or "amorphous" urea), whereas the one at 1645 cm^{-1} corresponds to urea groups in a more ordered structure. The remaining major peaks may be assigned as in the previous cases to N-H stretching (3290 cm^{-1}), C-H stretching (3000-2800 cm^{-1}), residual NCO (2276 cm^{-1}), aromatic ring stretching (1591 cm^{-1}), and N-H deformation plus C-N stretching (1543 and 1220 cm^{-1}).

Because of the difficulty of preparing TDI/water products of controlled composition, a fourth experiment was performed in which mixtures were prepared with a composition similar to that used for the normal foams, except that the polyol was replaced by a silicone fluid (Union Carbide Silicone Surfactant L-5340). This fluid has a very low hydroxyl content, so it remains effectively inert and urethane formation is negligible. Four mixtures were prepared, with TDI indices of 85, 100, 115, and 130. The products were rather sticky, friable foam-like materials with very little structural integrity. Nevertheless, with care, pieces could be cut and measured by the same ATR technique used for the regular foams, and the spectra were treated in much the same way, with normalization based on the silicone peak at 1092 cm^{-1}. The spectrum for index 100 is shown in Figure 10 together with that of the silicone fluid; the spectra for the other indices are qualitatively similar. Since the silicone fluid has no significant peaks in the 1800-1500 cm^{-1} region, the peaks observed in this region in the other spectra may be assigned to the polyurea. In this case there is a sharp peak at 1638 cm^{-1}, attributable to crystalline urea, and a smaller peak at 1708 cm^{-1}, attributable to amorphous urea (14,15). The height of both peaks increases with TDI index, as expected. The same is true for the N-H peak at 3278 cm^{-1} and the NCO peak at 2274 cm^{-1}. As in the second experiment discussed above, the carbonyl peak at 1708 cm^{-1} is of particular interest. As shown in Figure 11 (A), the shape is similar for all four spectra. However, very close examination shows slight differences, and when the "Index 85" spectrum is subtracted from the others, as shown in Figure 11 (B), a residual peak is observed at 1718 cm^{-1} and its intensity increases with increasing index. It is probable that this peak arises from biuret groups formed in increasing numbers as the TDI index is increased.

B) Foam Spectra

Eleven foams prepared with TDI indices ranging from 85 to 135 were examined by IR as described previously. The differences observed between the two spectra recorded for a given foam were small in comparison to the differences observed among the different foams, so each pair of spectra was co-added to give an "average" spectrum for each foam. This gave a total of eleven spectra for analysis, of which five are displayed in Figure 12. As mentioned in the Experimental Section, these have been corrected and normalized to give an absorbance of 1 for the strongest peak, the polyol C-O stetching band at 1089 cm^{-1}. Some variations in intensity are observed for the other peaks, and these were investigated quantitatively.

The following peaks are sufficiently well separated so that their area could be calculated by integration with the Nicolet software, using the frequency limits given in parentheses for drawing a baseline: (i) the N-H stretching peak at 3278 cm^{-1} (3430-3115 cm^{-1}); (ii) the C-H stretching peaks (3012-2550 cm^{-1}), which arise mainly from the polyol chains; (iii) the NCO stretching peak at 2272 cm^{-1} (2334-2150 cm^{-1}). The C-H peak area was then used as a reference to calculate NH/CH and NCO/CH ratios. As the C-H peak arises mainly from polyol, its area is more or less constant, since the spectra are normalized with respect to the polyol peak at 1089 cm^{-1}. Since the NH and the NCO groups originate from TDI, one would expect the NH/CH and NCO/CH ratios to increase as the TDI index increases. The behaviour is shown in Figure 13. The NH/CH ratio increases significantly with index up to about 115, then levels off. The residual isocyanate, on the other hand, is more or less constant up to 115, then shows a substantial increase. (In an earlier publication (6) involving a more limited set of foams, we observed an increase in the NCO/CH ratio over the range of indices 100 to 115. The difference is attributed to somewhat higher reactivity in the present series. In all other respects, the two series show excellent agreement.)

Other interesting peaks could not be integrated because of overlap, but their heights were recorded. Since the spectra are normalized to give a polyol peak height of 1, these peaks are effectively adjusted in height against the polyol peak. They include: (i) the carbonyl peak at around 1725-1710 cm^{-1} (the exact position varies somewhat because there is more than one component); (ii) the crystalline urea carbonyl peaks at 1637 cm^{-1}; (iii) the aromatic ring stretching peak at 1595 cm^{-1}. The behaviour observed for these peaks is shown in Figure 14. The aromatic ring peak shows a steady increase with index, as expected. However, the other two show an abrupt change around index 115. The carbonyl peak at 1725-1710 cm^{-1} has approximately constant height up to this point, then increases substantially. The crystalline urea peak at 1637 cm^{-1}, on the other hand, increases steadily up to index 115, then decreases somewhat.

Figure 15 shows in detail the carbonyl region for all eleven spectra. It is seen that the band at 1725-1710 cm^{-1} consists of at least two components. At low index (85 to 105) the maximum occurs around 1725 cm^{-1}, but beyond this, the shoulder around 1710 cm^{-1} begins to dominate. Then at very high index the two appear to merge to give a broad band centered at around 1717 cm^{-1}.

CONCLUSION

Based on both the FT-IR and the exotherm data, a model is proposed for the foam formation process relative to a variation in the TDI index.

At TDI indices from 85 to 115, the TDI reacts almost completely in two main stages involving reactions with water and with polyol. From the NCO/CH peak area ratio, it is estimated that at least 98% of the NCO groups react (6,14). The TDI-polyol reaction produces urethane groups which absorb near 1730 cm^{-1}, if free, or closer to 1700 cm^{-1}, if hydrogen bonded (4). The TDI-water reaction produces polyurea structures whose carbonyl groups absorb at three different frequencies depending on the environment. These are 1705 cm^{-1} (highly amorphous structure), 1660 cm^{-1} (disordered crystalline structure), and 1637 cm^{-1} (highly crystalline structure) (14,15,18). As the TDI index increases from 85 to 115, the carbonyl peak at 1725-1710 cm^{-1} remains approximately constant in height, but its shape changes somewhat. This reflects an increase in the contribution from the peak at around 1710 cm^{-1} (hydrogen-bonded urethane or "amorphous" urea) compared to that from the free urethane groups at around 1725 cm^{-1}. At the same time, both the "crystalline urea" peak at 1637 cm^{-1} and the N-H stretching peak near 3300 cm^{-1} show a substantial increase.

At index 115, a change occurs. The TDI begins to have difficulty finding enough OH groups to react with, so the amount of unreacted NCO groups shows an increase. However, the increase is not as drastic as expected because a large part of the excess TDI undergoes further reaction, as shown by a new exothermic peak. This peak gives rise to a second plateau in the temperature versus time curve (Fig. 2). It presumably involves reaction between NCO groups and ureas to form biurets. (The reaction between NCO and urethane to form allophanate is also possible but is less important because the number of urea N-H groups exceeds the number of urethane N-H groups by more than 5 to 1.) In the IR spectrum, the N-H stretching band intensity levels off because the urea-biuret conversion does not increase the number of N-H bonds. However, it does produce new carbonyl bonds absorbing at 1718 cm^{-1}, and this causes a significant increase in absorption at this frequency. Also, the biuret groups interfere with the crystallization of the urea groups. Thus there is a drop in the intensity of the "crystalline urea" peak at 1637 cm^{-1}. The maximum crystalline urea content occurs at index 115, and one would expect this to influence the mechanical properties of the foam (3).

SUMMARY OF FINDINGS

- Above index 105, a third peak appears in the derivative curve.
- Infrared spectral analysis indicates that this last exothermic peak is related to the formation of biuret cross-links.
- The crystalline urea content is at a maximum at index 115.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

1. Typical temperature vs time curve with 2 plateaus (far above) and temperature derivative with respect to time vs time (above).

2. Variation of exotherm maxima on the temperature vs time curve as a function of TDI index.

3. Maximum rates of temperature rise as a function of TDI index.

4. Peak width at half height for the third peak in the derivative trace as a function of TDI index.

5. Time of occurrence of the maxima in the derivative trace as a function of TDI index.

6. ATR spectra of a mixture of TDI and N.P. 16-46: (A) initial spectrum; (B) after one day at 23°C; (C) difference spectrum of (B) minus (A).

7. Transmission spectra of the reaction products of phenyl isocyanate and N.P. 16-46.

8. (A) detail of the carbonyl region of the phenyl isocyanate/N.P. 16-46 reaction products; (B) detail of the same region of the difference spectrum.

9. Diffuse reflection spectrum of the solid obtained from the reaction of TDI and water.

10. (A) spectrum of a polyurea foam prepared in a surfactant at I: 100; (B) spectrum of the surfactant.

11. (A) detail of the carbonyl region of four polyurea foams obtained at the indicated indices; (B) subtraction spectra.

12. Typical foam spectra.

13. Variation of the NH and NCO stretching peak areas as a function of index.

14. Variation of peak heights obtained at the indicated frequencies as a function of index.

15. Detail of the carbonyl region of the spectra obtained from the eleven foams.

BIOGRAPHIES

Kenneth Cole

Kenneth Cole is a Research Scientist in the Chemistry and Corrosion Group of the Industrial Materials Research Institute. He obtained a B.Sc. at Memorial University of Newfoundland, followed by a Ph.D. in Chemistry at McGill University, and worked for six years in industrial chemicals R&D before joining IMRI in 1981.

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Corinne Dueck is a Development Specialist with Union Carbide Canada Limited and works in the area of urethane intermediates for flexible slabstock foam. She obtained her B.Eng. and M.Eng. in Chemical Engineering from McGill University before joining UCCL in 1985.

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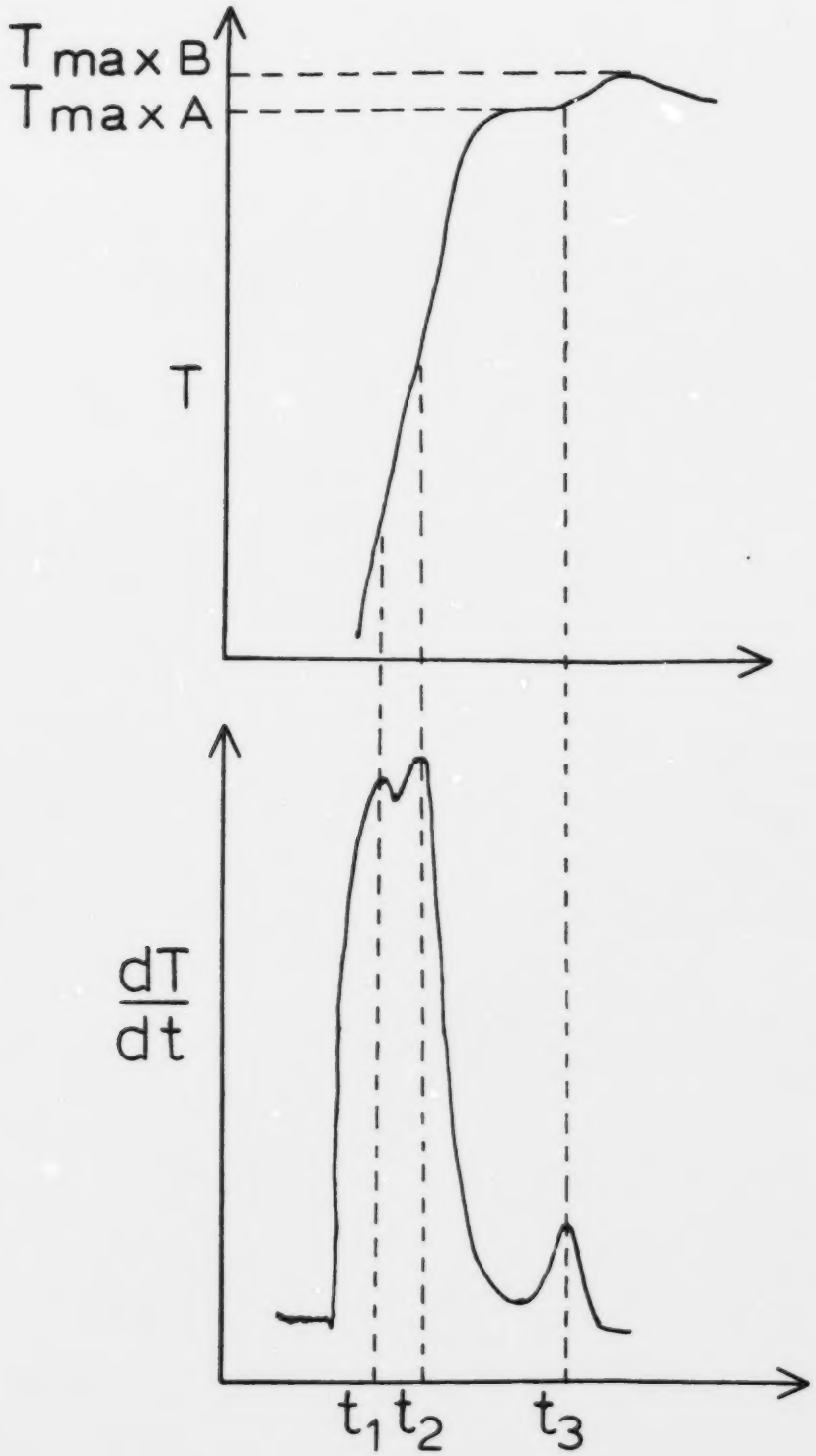
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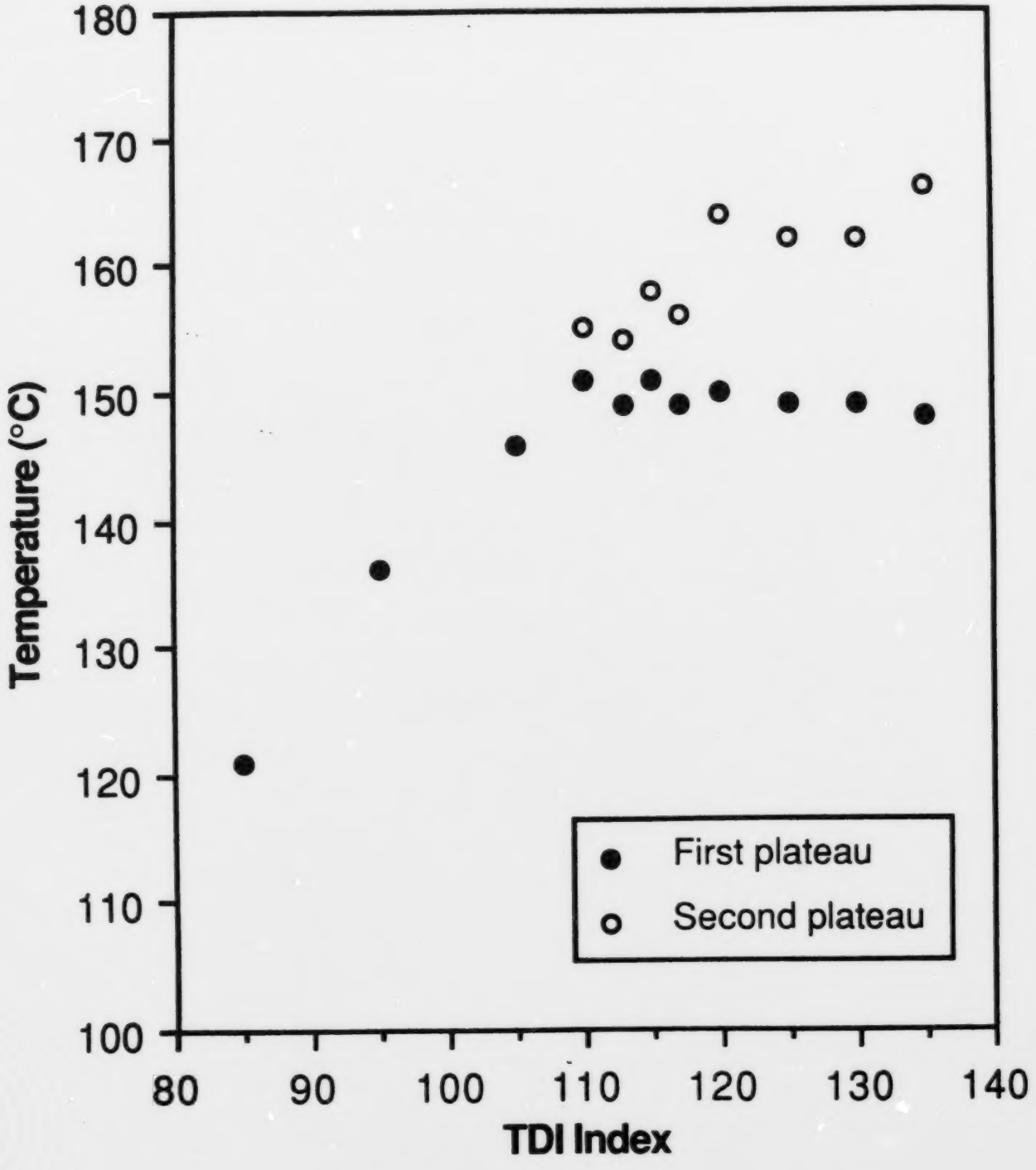
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170
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150
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110
100
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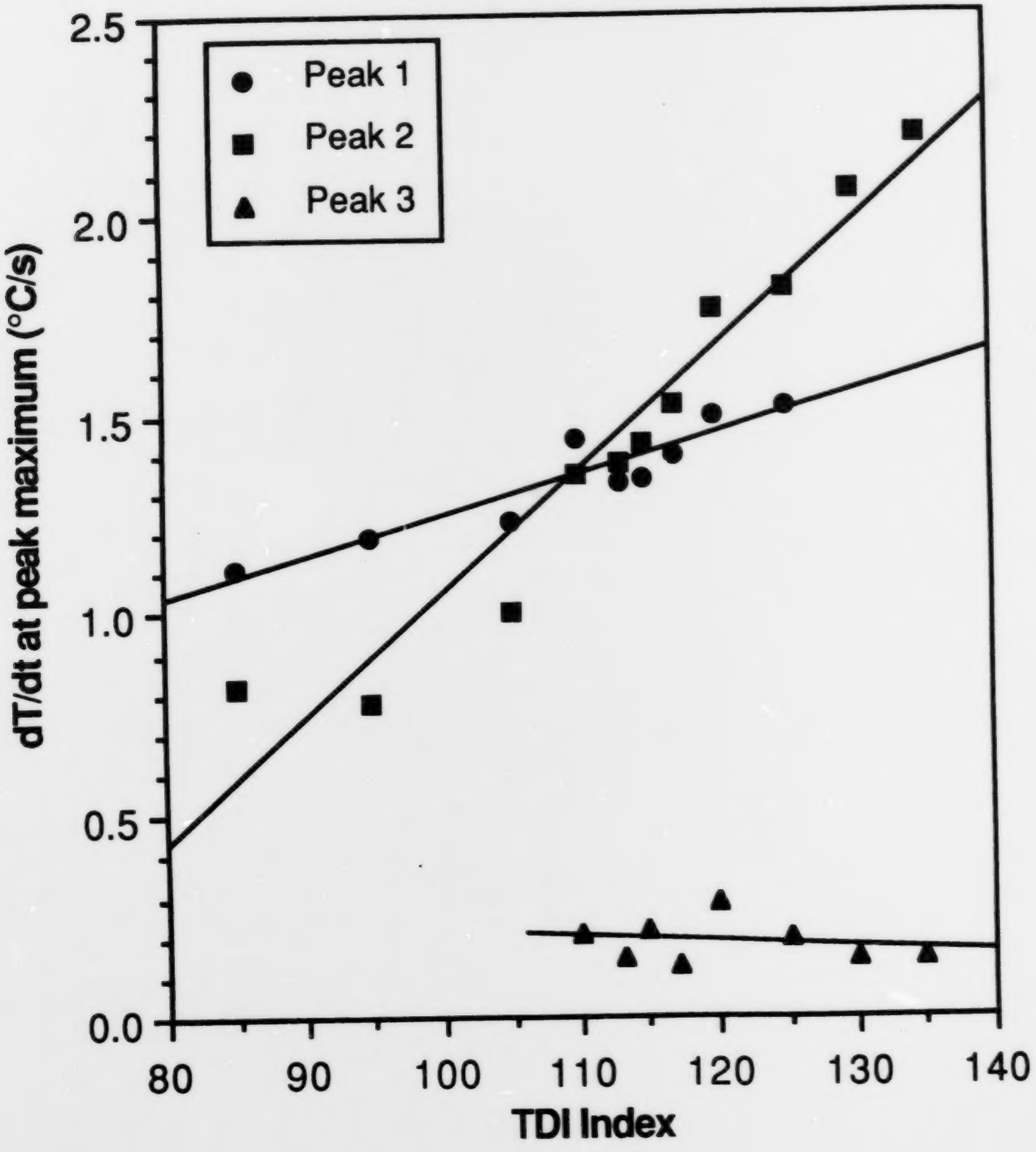
100
110
120
130
140
TDI Index
First plateau
Second plateau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Peak 2
Peak 3
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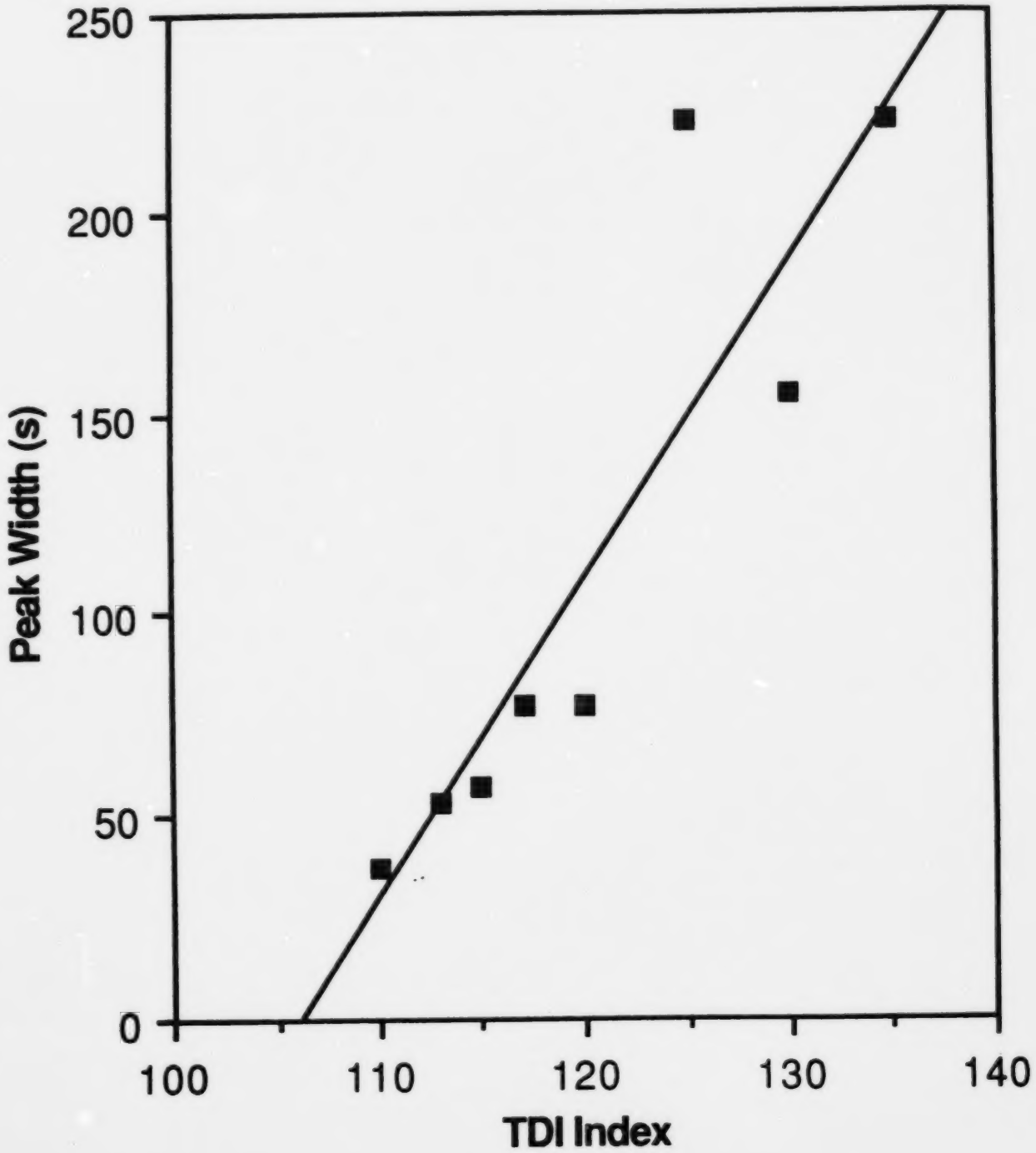
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Peak Width (s)
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120
130
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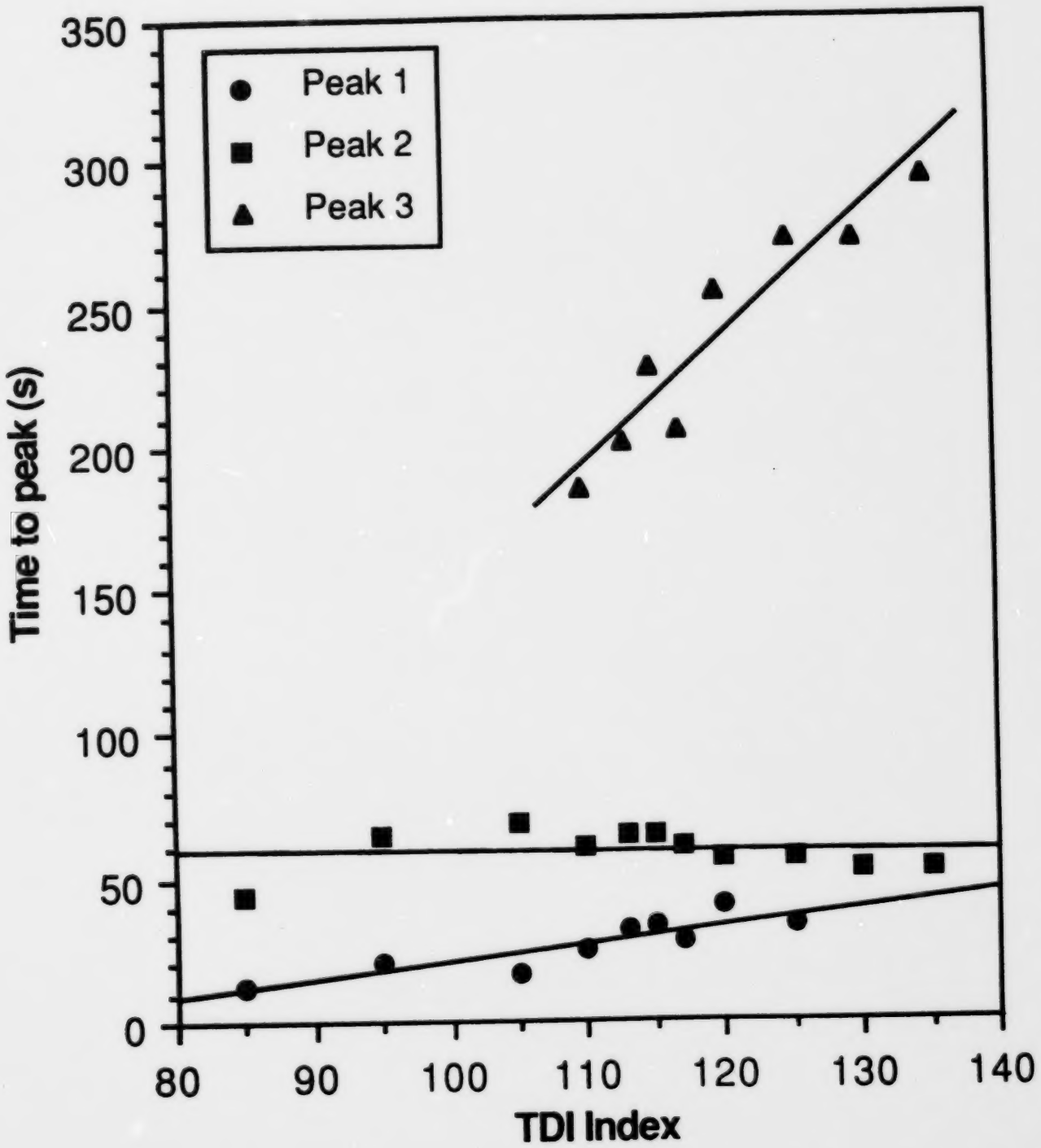
TDI Index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Peak 2
Peak 3
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50
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80
90
100
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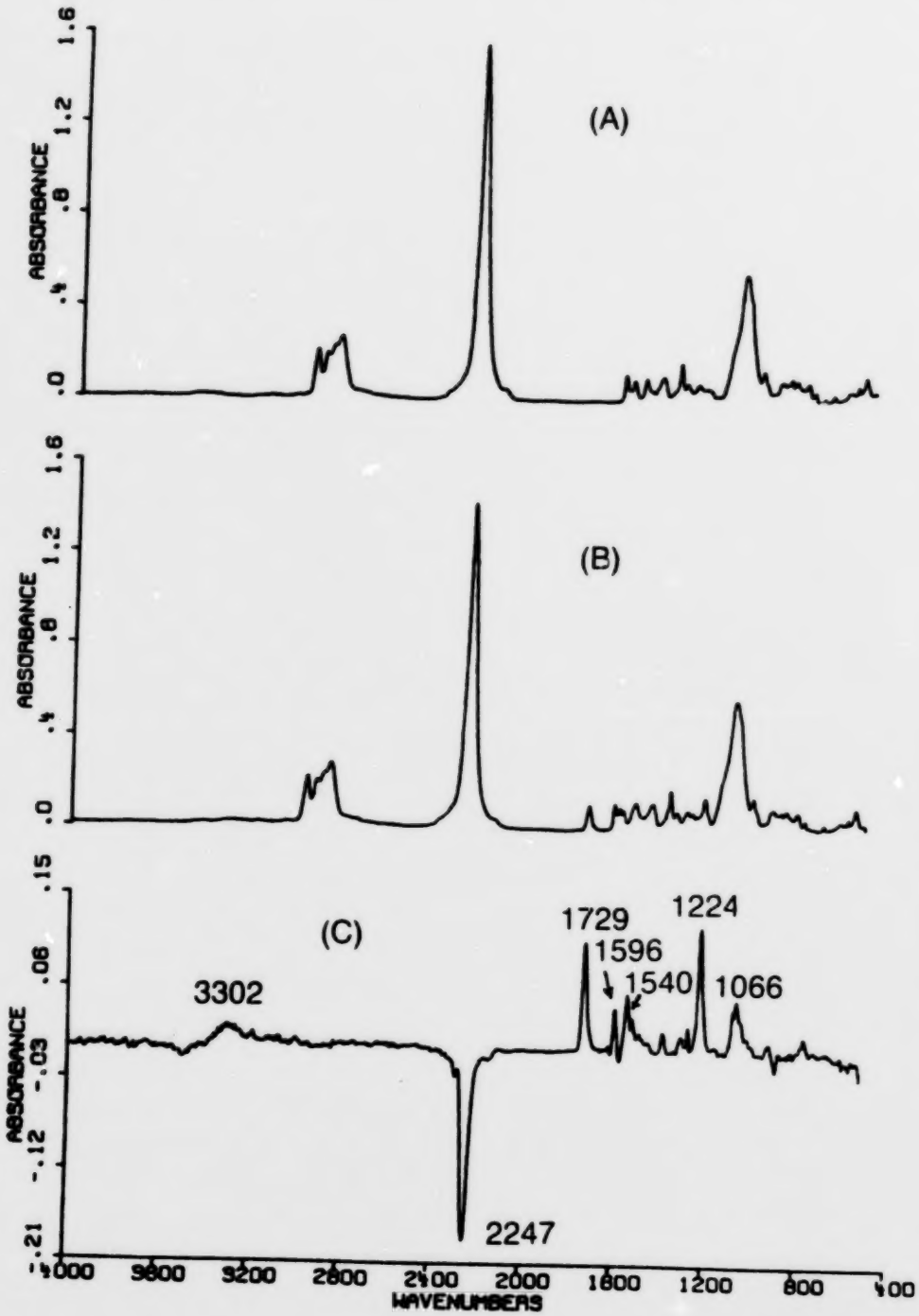
120
130
140
TDI Index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(B)
(C)
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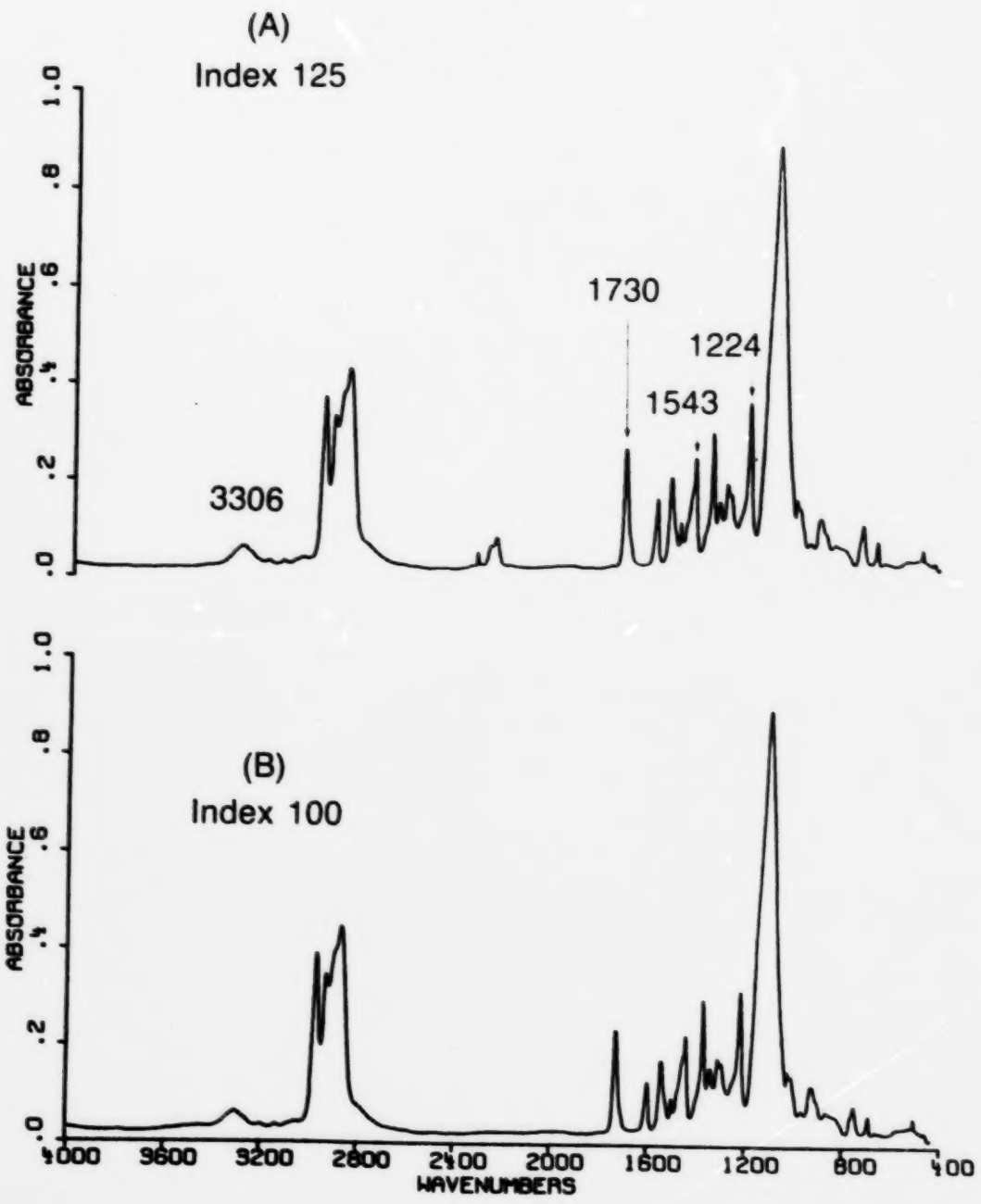
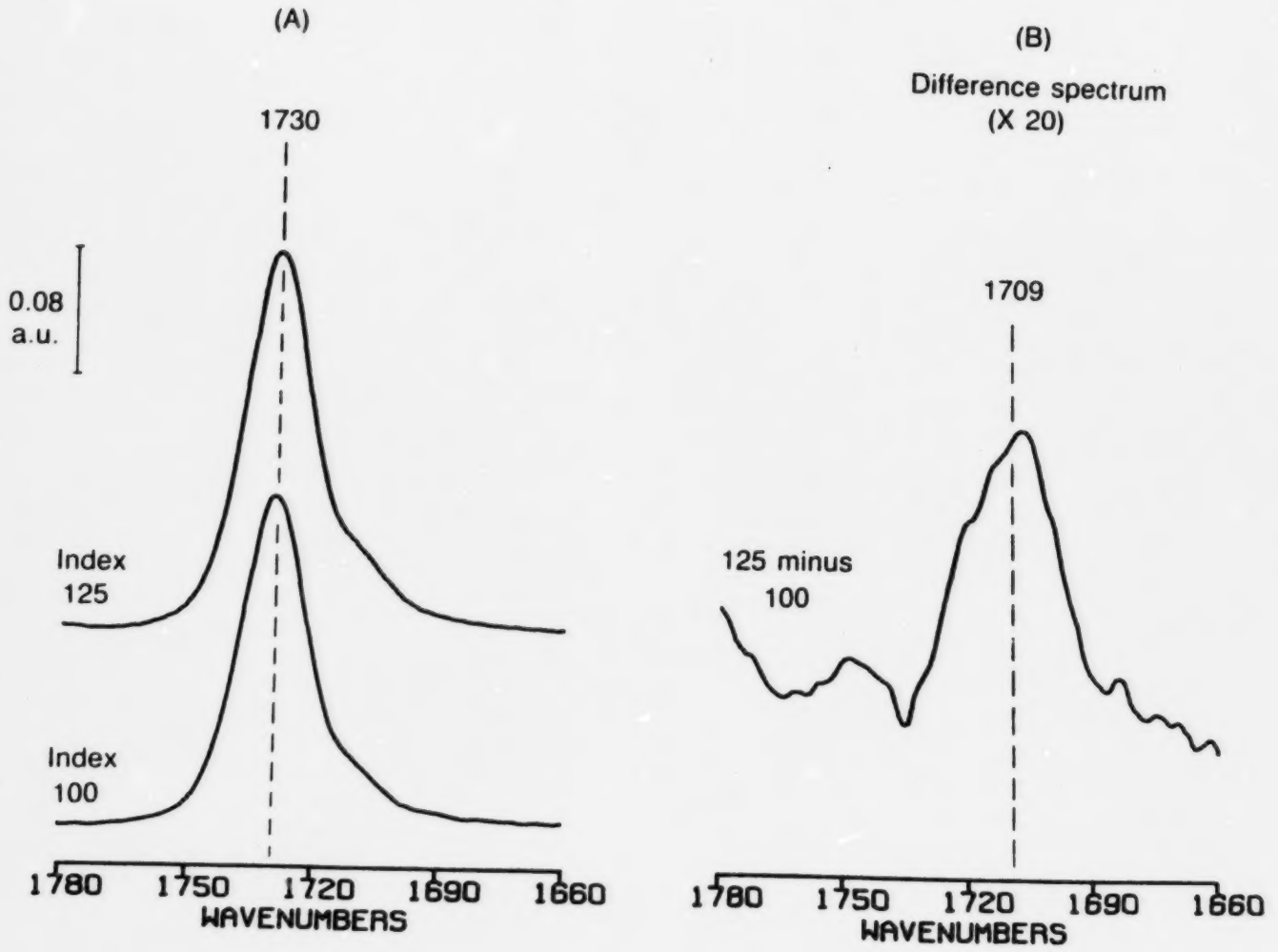
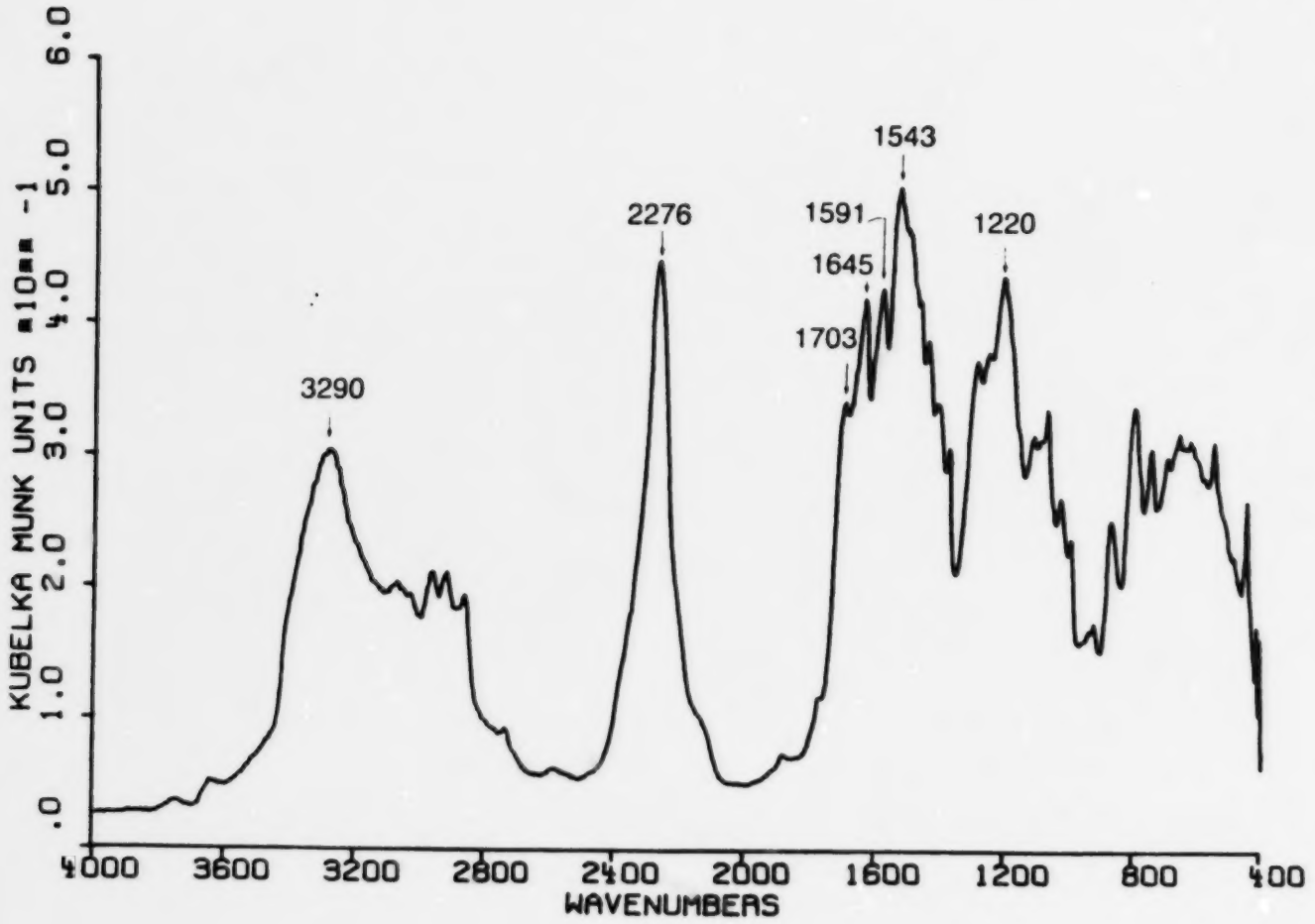
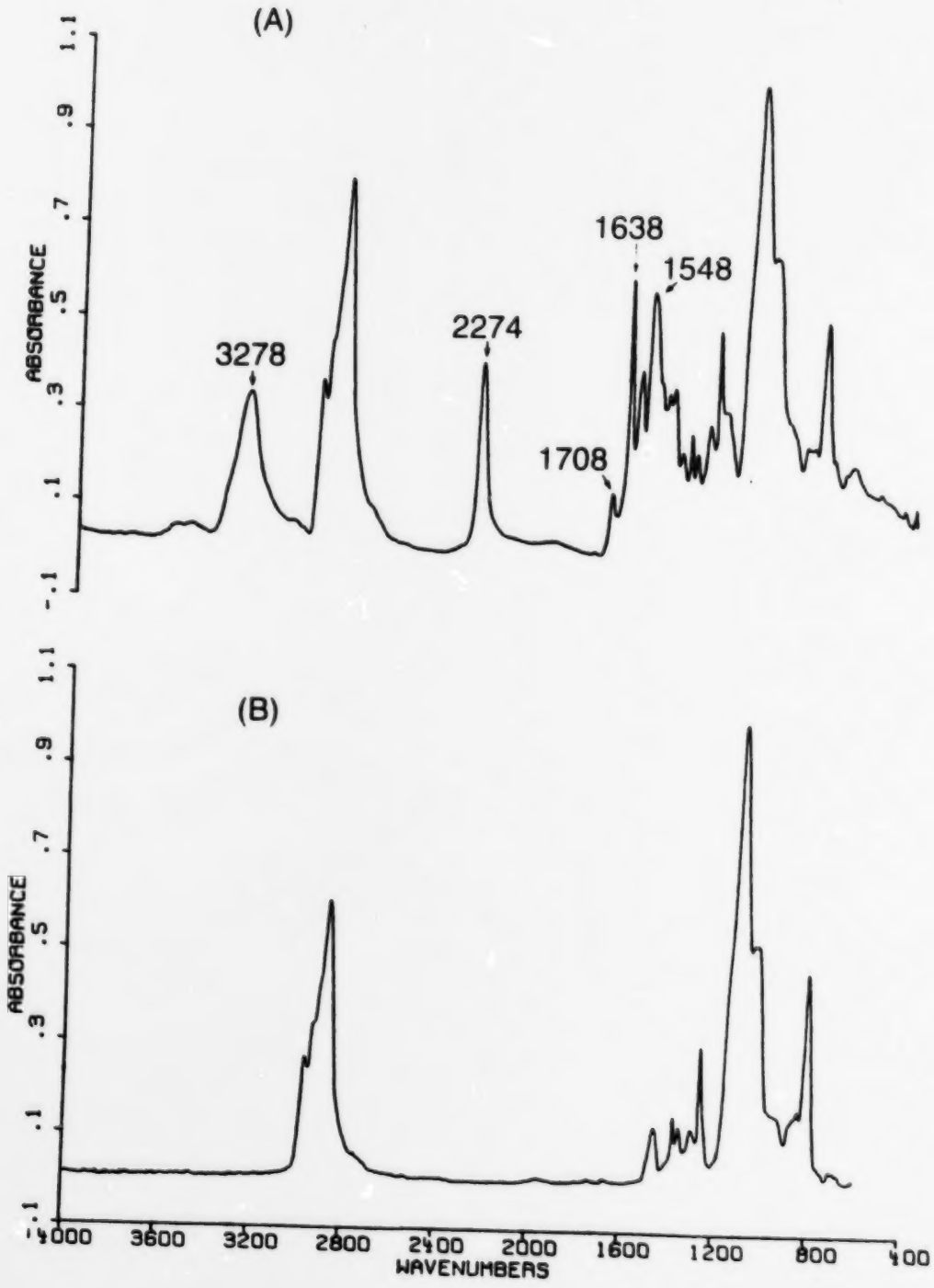
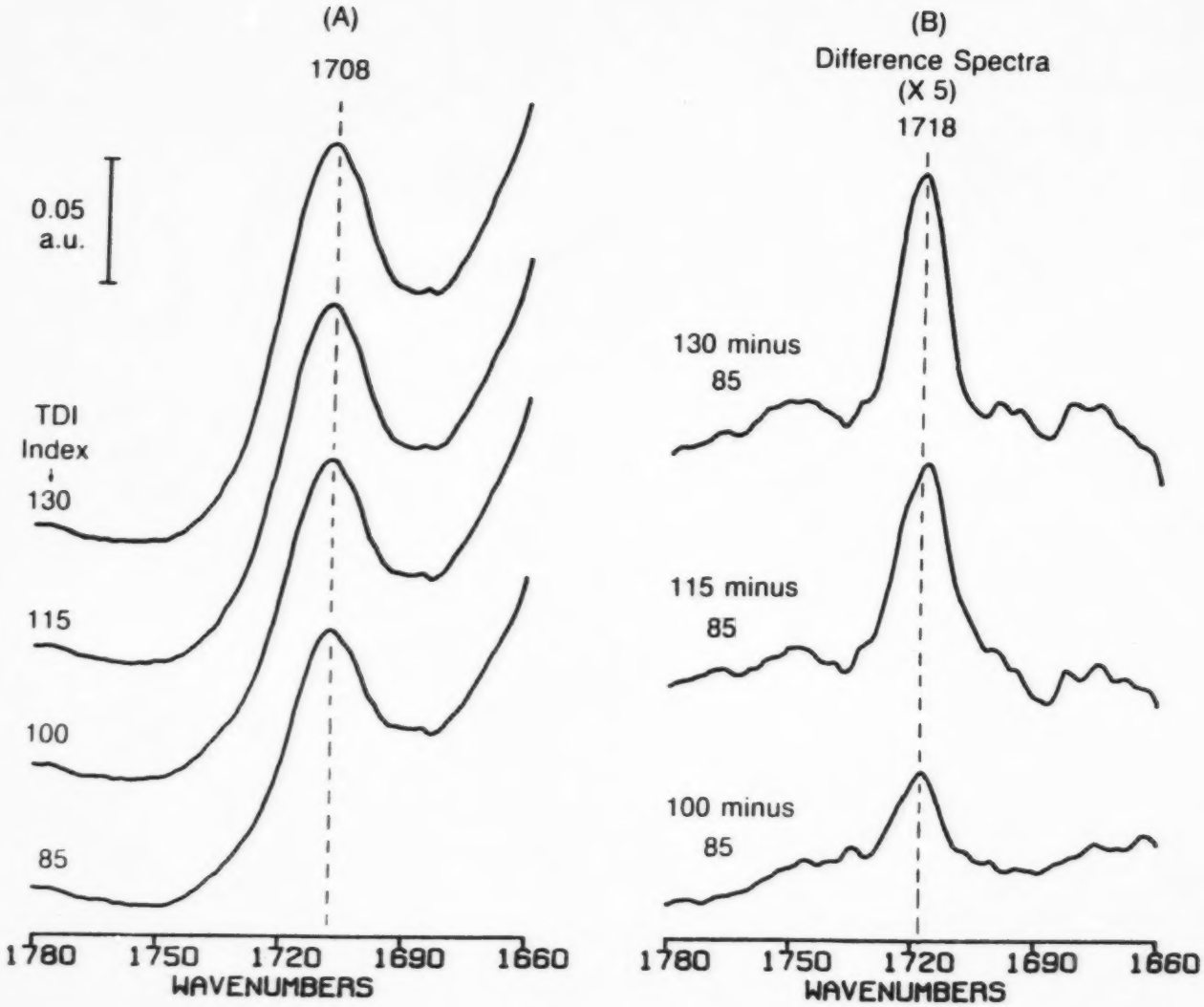
WAVENUMBERS

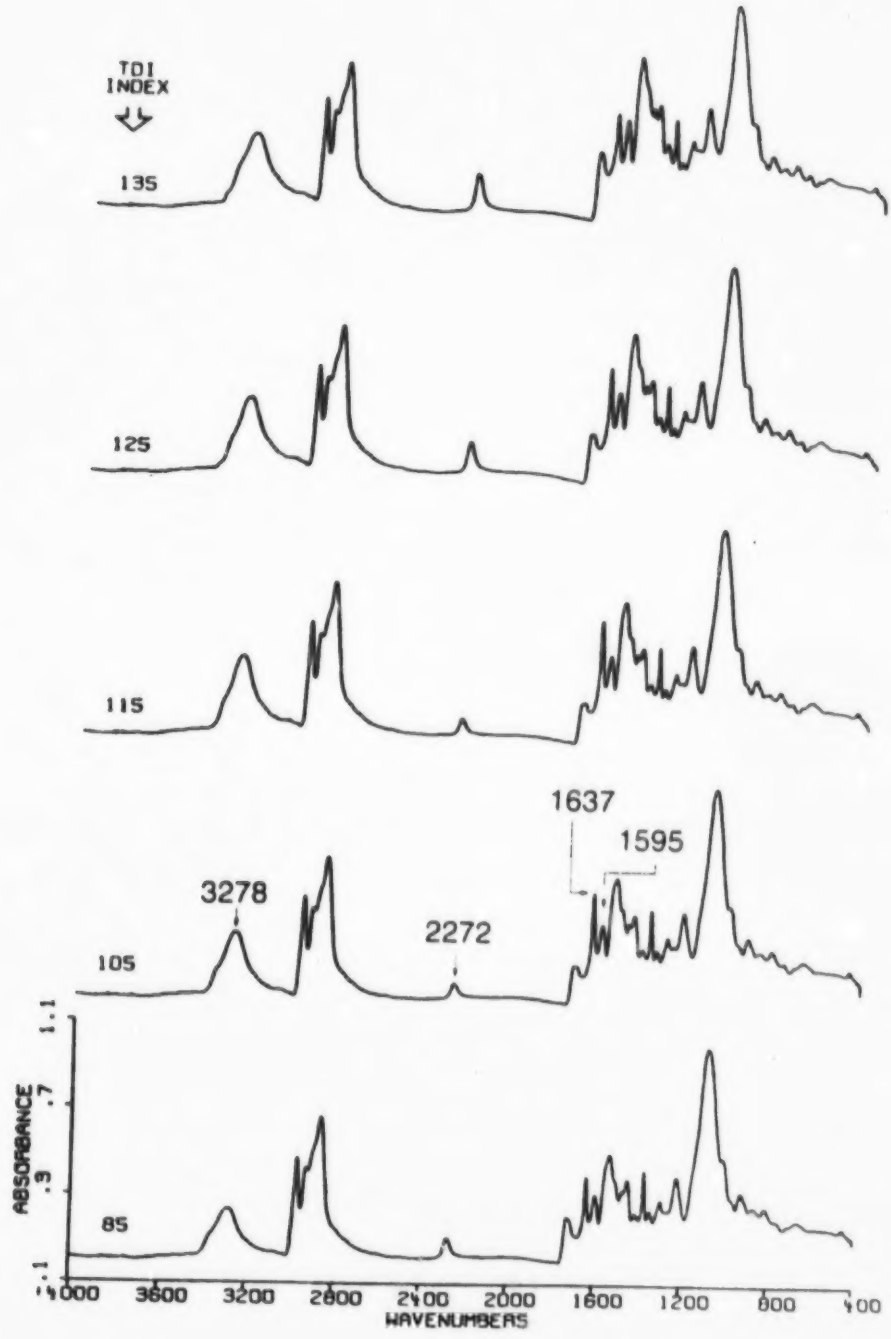

(A)
Index 125
ABSORBANCE
.0
.2
.4
.6
.8
1.0
3306
1730
1543
1224
(B)
Index 100
ABSORBANCE
.0
.2
.4
.6
.8
1.0
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS

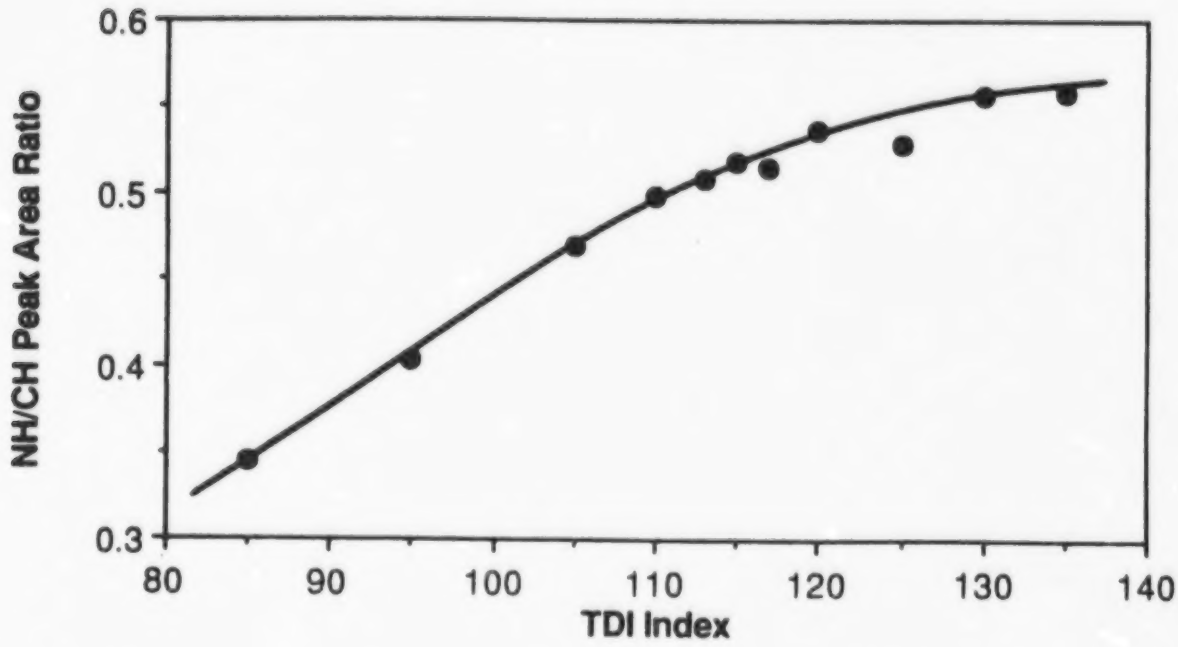

(A)
1730
0.08
a.u.
Index
125
Index
100
1780
1750
1720
1690
1660
WAVENUMBERS
(B)
Difference spectrum
(X 20)
1709
125 minus
100
1780
1750
1720
1690
1660
WAVENUMBERS

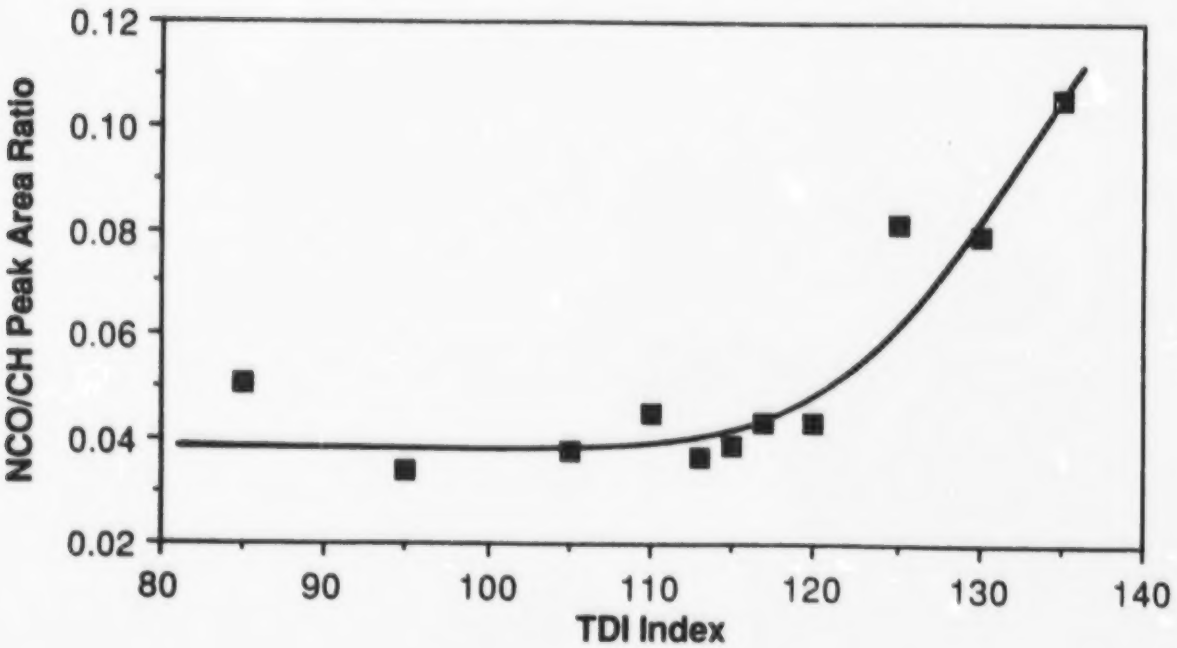

KUBELKA MUNK UNITS *10** -1
.0
1.0
2.0
3.0
4.0
5.0
6.0
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS
3290
2276
1703
1645
1591
1543
1220

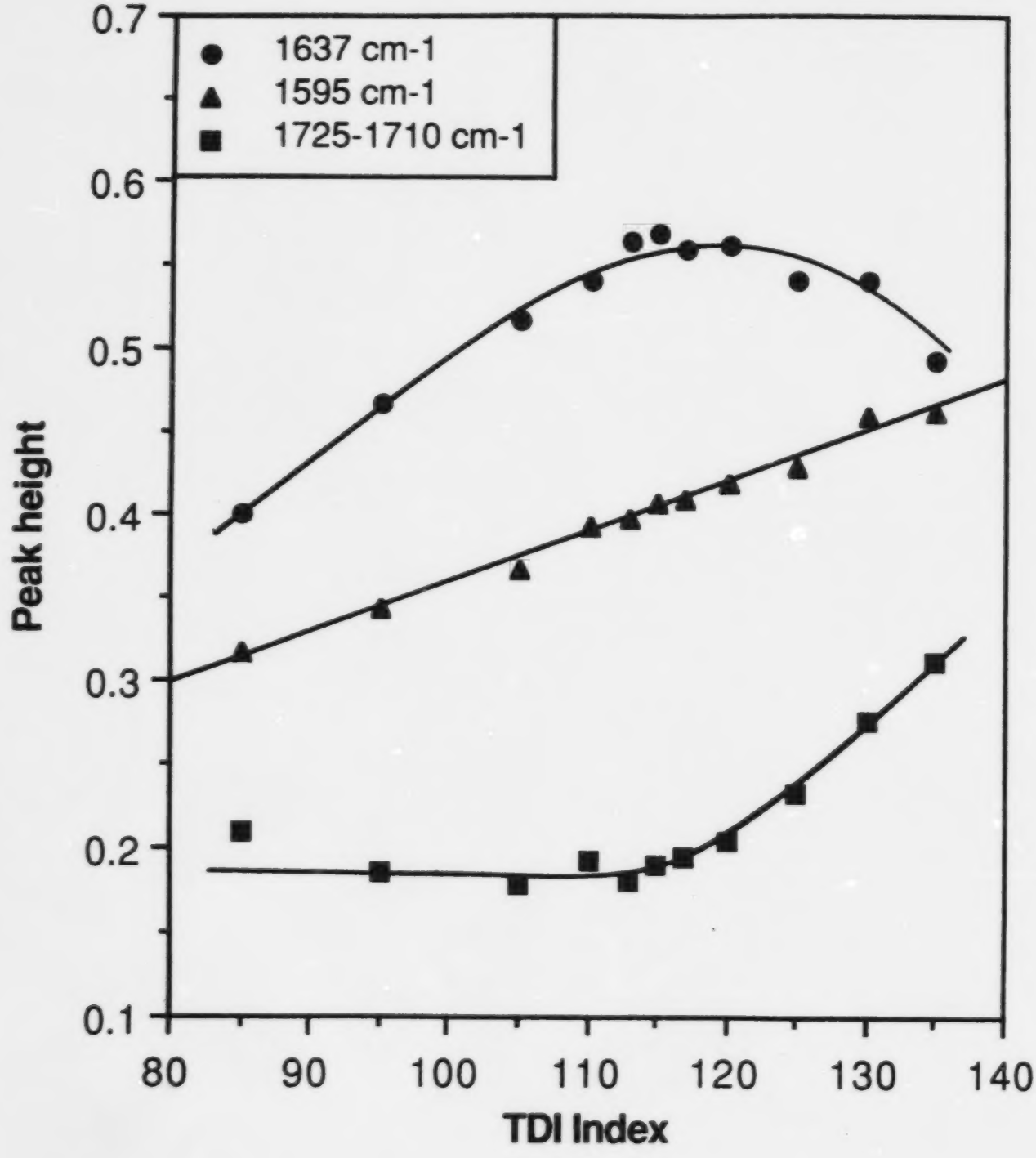

(A)
ABSORBANCE
1.1
.9
.7
.5
.3
.1
-.1
3278
2274
1708
1638
1548
(B)
ABSORBANCE
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS

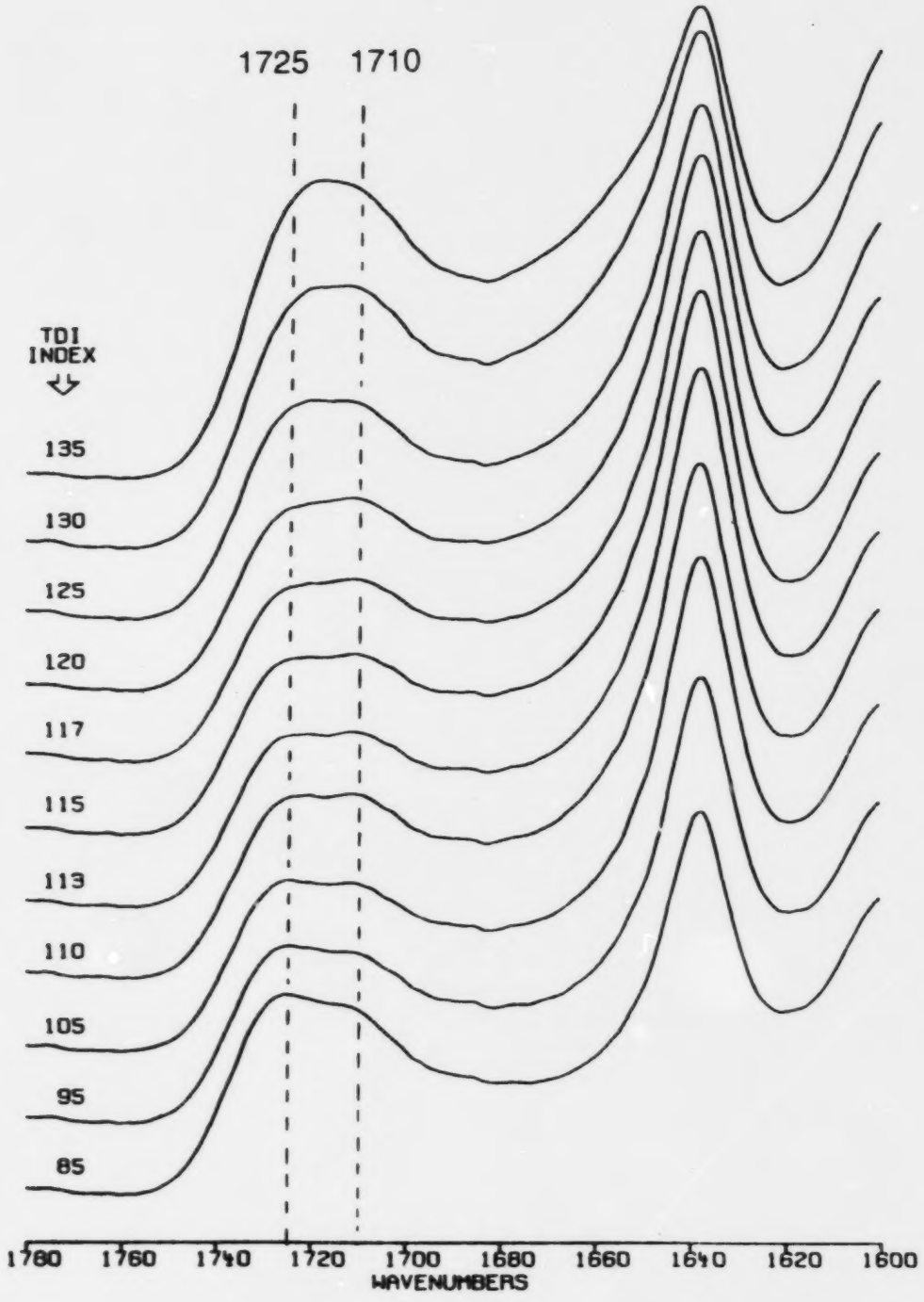

(A)
1708
0.05
a.u.
TDI
Index
130
115
100
85
1780
1750
1720
1690
1660
WAVENUMBERS
(B)
Difference Spectra
(X 5)
1718
130 minus
85
115 minus
85
100 minus
85
1780
1750
1720
1690
1660
WAVENUMBERS


TDI
INDEX
135
125
115
105
85
1637
1595
3278
2272
ABSORBANCE
1.1
.7
.3
.1
4000
3600
3200
2800
2400
2000
1600
1200
800
400
WAVENUMBERS


NH/CH Peak Area Ratio
0.6
0.5
0.4
0.3
80
90
100
110
120
130
140
TDI Index


NCO/CH Peak Area Ratio
0.12
0.10
0.08
0.06
0.04
0.02
80
90
100
110
120
130
140
TDI Index


1637 cm-1
1595 cm-1
1725-1710 cm-1
Peak height
0.7
0.6
0.5
0.4
0.3
0.2
0.1
80
90
100
110
120
130
140
TDI Index


1725
1710
TDI
INDEX
135
130
125
120
117
115
113
110
105
95
85
1780
1760
1740
1720
1700
1680
1660
1640
1620
1600
WAVENUMBERS